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Elastic, mechanical and thermodynamic properties of zinc blende III-X (X= As, Sb): ab-initio calculations

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Abstract – *In this work, density functional theory plane-wave full potential method, with local density approximation (LDA) are used to investigate the structural, mechanical and thermodynamic properties of of zincblende III-X (X= As, Sb) compends. Comparison of the calculated equilibrium lattice constants and experimental data shows very good agreement. The elastic constants were determined from a linear fit of the calculated stress-strain function according to Hooke's law. From the elastic constants, the bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio σ, anisotropy factor A, the ratio B/G and the hardness parameter H for zincblende III-X (X= As, Sb) compound are obtained. Our calculated elastic constants indicate that the ground state structure of III-X (X= As, Sb) is mechanically stable. The sound velocities and Debye temperature are also predicted from elastic constants.*

Keywords: *Mechanics, Mechanics, energy, DFT, LDA*
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I. Introduction

The method developed by Charpin (modified by Ferenc Karsai) and integrated in WIEN2k code [1] has been used to obtain elastic constants of considered binary compounds. The knowledge of elastic parameters of solids is very important because they provide important information about the stability and mechanical properties of solids such as sound velocities, load deflection, fracture toughness, thermoelastic stress and internal strain etc.

II. Elastic and mechanical properties

The elastic constants Cklmn (where the letter k, l, m, n refer to Cartesian components) are defined by the help of a Taylor expansion of the total energy of the system, E(V,ϵ), in accordance with a small strain ϵ of the lattice (V is the volume of the system). The energy E(V,δ) fit curve versus strain, δ, for the three different types of strains, namely the volume conserved, tetragonal and rhombohedral shear strains, are plotted in Figure 1 (a)-(c), respectively, for the studied binary compounds. The total energy has been calculated for five to seven different distortions for each of the three different deformations of the lattice. There are 21 independent elastic constants Cij, but symmetry of the cubic lattice reduces this number to only 3 independent constants (C_{11},C_{12}, and C_{44}) for cubic lattices. The calculated values of elastic constants are summarized in Table 1. The calculated elastic constant values of studied binary compounds are in good agreement with the results of other calculations [2, 4] and the available experimental data [3, 5].The obtained values for the elastic tensor constants satisfy the mechanical stability restrictionsfor cubic unit cells $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{12} < B < C_{11}$ [6].Resistance to shear distortions of a cubic crystal is best characterized by the two moduli the tetragonal shear constant $C' = (C_{11}-C_{12})/2$ and C_{44}. The elastic constant C_{44} is related to an orthorhombic deformation whereas C' is related to a tetragonal deformation. At any volume V, the bulk modulus B for a cubic crystal is related to elastic constants by $B_0 = (C_{11}+2C_{12})/3$ [7]. The C_{11} and C_{12} can be obtained from the calculated bulk modulus and C'.

The Kleinmann parameter [8], ζ, is an important parameter describing the piezoelectric effect of solids [9]. It is given by the following relation:

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}$$

The obtained values of ζ for the materials are between 0.575 and 0.716 as shown Table 1. The obtained results for studied binary compounds fairly coincide with previous first-principles calculations [2, 10].We have also found the anisotropy factor $A = 2C_{44}/(C_{11} - C_{12})$. For an isotropic crystal, A is equal to 1, while any value smaller or larger than 1 indicates anisotropy. From Table 1, it is clearly seen that the calculated anisotropy factor for these compounds deviate from 1. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal.

The isotropic bulk modulus B_0, which is related to C_{11} and C_{12}, and shear modulus (G) are determined by the calculated elastic constants [11]. However, there is no distinct expression for the polycrystal-averaged shear modulus with respect to the C_{ij}, but one can evaluate approximate averages of the lower and upper bounds given by various theories [12]. Voight [13] found upper bounds, while Reuss [14] discovered lower bounds for all lattice.

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The upper bound due to Voight is calculated as

$$G_V = (C_{11} - C_{12} + 3C_{44})/5$$

and the lower bound due to Reuss reads as

$$5/G_R = 4/(C_{11} - C_{12}) + 3/C_{44}$$

According to Hill [15], the arithmetic average of the Voight and Reuss values can be used as an estimated of the average shear modulus G=1/2 (GV+GR). Another important mechanical parameter that is directly correlated to the ductility is the Poisson's ratio and given by

$$v = \frac{3B - 2G}{2(3B + G)}$$

where Y is the Young's modulus and is related to the bulk and shear moduli

$$Y = \frac{9BG}{3B + G}$$

Y and v are frequently measured for polycrystal materials when investigating their hardness. Young's modulus is a measure of the stiffness of a given material, whereas Poisson's ratio is the ratio (when a sample is stretched) of the contraction or transverse strain to the extension or axial strain.The calculated average shear modulus (G), Young's modulus (Y) and Poisson's ratio (v) are given in Table 1. The obtained results for studied binary compounds fairly coincide with previous first-principles calculations [2, 10] and experimental results [16, 17]. Materials with high G are likely to be hard materials. In studied compounds, GaAs exhibits the largest value of G (54.551 GPa) being the most incompressible of all. The Young modulus (Y) determines the stiffness of the material, i.e., the larger value of Y, the stiffer is the material [18] and the stiffer solids have covalent bonds [19].It can be seen from Table 1 that the largest value of Y (130.388 GPa) being the most stiffer of all occurs for GaAs implying it to be more covalent in nature as compared to other studied compounds.

The proportion between bulk modulus and average shear modulus (B_0/G) has been proposed by Pugh [20] to roughly determine the ductile or brittle character of a material. The critical value which separates ductile and brittle material is 1.75; i.e., if B_0/G is smaller than 1.75, then the material behaves in a brittle manner; otherwise it

will be of ductile nature [21]. The B_0/G ratio of studied materials is presented in Table 1.

The Cauchy pressure is another interesting elastic parameter which describes the angular characteristic of atomic bonding in a material can be calculated by using the following relation [23]:

$$C' = C_{12} - C4_4$$

Table 1 Calculated elastic constants (C_{11}, C_{12} and C_{44}) and tetragonal shear constant (C'), Kleinman's internal-strain parameter (ζ), shear modulus anisotropy (A), the average shear modulus (G), Young's modulus (Y) and Poisson's ratio (ν), and B_0/G ratio of studied materials and the comparison of these quantities with available theoretical and experimental data.

Comp.	C11 (GPa)	C12 (GPa)	C44 (GPa)	C'	B0 (GPa)	ʒ	A	G (GPa)	Y (GPa)	ν	B0/G
AlAs	110,442 113.1 [2] 119.9 [3]	56,982 55.5 [2] 57.5 [3]	78,132 54.7 [2] 56.6 [3]	26,730 28.8 [2]	74,802	0,638 0.592 [2] 0.481 [10]	2,923 1.899 [2]	50,867 77.14 [10]	124,402 175.39 [10]	0,22 30.329 [2] 0.136 [10]	1,471 1.043 [10]
GaAs	113,589 115,1 [4] 118.1 [5]	50,115 51.5 [4] 53.2 [5]	78,401 56.8 [4] 62.0 [5]	31,737 36.4 [2]	71,273 72.7[4]	0,575 0.506 [2]	2,470 1.742 [2]	54,551 32.6 [16]	130,388 85.5 [16]	0,195 0.293 [2] 0.31 [17]	1,307
InAs	81,547 92.2 [2] 83.3 [5]	49,809 46.5 [2] 45.3 [5]	60,838 44.4 [2] 39.6 [5]	15,869 22.9 [2]	60,388	0,716 0.598 [2]	3,834 1.943 [2]	35,683	89,433	0,253 0.335 [2]	1,692
AlSb	84,615 85.5 [2] 89.4 [5]	42,727 41.4 [2] 44.3 [5]	60,737 39.9 [2] 41.6 [5]	20,944 22.1 [2]	56,690	0,629 0.601 [2]	2,900 1.81 [2]	39,665	96,490	0,216 0.326 [2]	1,429
GaSb	84,169 92.7 [2] 88.4 [5]	38,939 38.7 [2] 40.3 [5]	59,841 46.2 [2] 43.2 [5]	22,615 27 [2]	54,016	0,593 0.530 [2]	2,646 1.711 [2]	40,517	97,238	0,200 0.295 [2]	1,333
InSb	65,062 72.0 [2] 66.7 [5]	38,348 35.4 [2] 36.5 [5]	50,121 34.1 [2] 30.2 [5]	13,357 18.3 [2]	47,253	0,699 0.603 [2]	3,752 1.863 [2]	29,636	73,535	0,241 0.487 [2]	1,594

It is clearly seen from this table that B_0/G ratio of considered structures should be classified as brittle character.

To obtain the stiffness of these compounds, the microhardness parameter (H) is also calculated using the following equation [22]:

$$H = \frac{(1-2\nu)Y}{6(1+\nu)}$$

The calculated H values are 9.40GPa, 11.09GPa, 5.87GPa, 7.50GPa, 8.10GPaand 5.12forAlAs, GaAs, InAs, AlSb, GaSb and InSb at zero pressure, respectively.

The positive value of Cauchy pressure is responsible for a ionic bonding while a negative Cauchy pressure, however, requires an angular or directional character in the bonding (covalent bonding). The more negative the Cauchy pressure, the more directional and of lower mobility the bonding. Moreover, a material with more negative value of Cauchy pressure will have more brittle nature. The calculated values of C' are summarized in Table 2, which indicate that the sign of the Cauchy pressure is negative for all studied materials. The kind of bonds can be also determined by means of the value of Poisson's ratio (υ). The value of Poisson's ratio is nearly 0.25 or more for a typical ionic material, while it is much less than 0.25 (around 0.1) for a typical covalent

compound [24]. As indicated Table 1, our calculation shows that υ < 0.25 for all studied materials. Consequently, our Cauchy pressure calculations are consistent with our Poisson's ratio values.

Table 2.Calculated microhardness parameter (H), Cauchy pressure (C''), and 1st and 2nd Lame constants (λ, μ), wave velocities (v_t, v_l and v_m), Debye temperature (θ_D), melting point (T_m) and the minimum thermal conductivity (κ_{min}) of studied materials.

Comp.	H (GPa)	C" (GPa)	λ (GPa)	μ (GPa)	v_t (m/s)	v_l(m/s)	v_m (m/s)	Θ_D (K)	T_m (K)±300	κ_{min} (WmK^{-1})
AlAs	9,40	-21,150	40,891	50,867	3680,935	6163,647	4073,853	428,576	1205,712	1,769
GaAs	11,09	-28,286	34,905	54,551	3193,605	5188,860	3523,838	371,173	1224,314	1,534
InAs	5,87	-11,029	36,599	35,683	2501,806	4351,768	2778,513	273,101	1034,942	1,053
AlSb	7,50	-18,009	30,247	39,665	3036,484	5046,935	3358,187	325,907	1053,074	1,241
GaSb	8,10	-20,901	27,005	40,517	2678,678	4374,136	2957,205	288,857	1050,442	1,107
InSb	5,12	-11,773	27,496	29,636	2258,360	3864,231	2504,483	230,170	937,519	0,830

The other interesting elastic parameters are Lame constants (λ, μ) which depend on a material and its temperature. These parameters are related to the Young modulus and Poisson's ratio by using the following equations:

$$\lambda = \frac{Y\upsilon}{(1+\upsilon)(1-2\upsilon)} \text{ and } \quad \mu = \frac{Y}{2(1+\upsilon)}$$

where Y is the Young's modulus and υ Poisson's ratio. Our calculated values of λ and μ are summarized in Table 2. The two parameters together constitute a parametrization of the elastic moduli for homogeneous isotropic media, λ is known as Lame's first constant and μ is Lame's second constant. The Lame's first modulus, λ, is related to a fraction of Young's modulus. For an isotropic system one can show that $\lambda=C_{12}$ and $\mu= C'$ [25]. As shown from Table 1 (from anisotropy factor, A) the studied materials are strongly anisotropic character; therefore our obtained results do not satisfy the later relations, which are valid only for the isotropic systems, which is in agreement with the obtained results.

III. Thermodynamic properties

The Debye temperature (θ_D) which is a significant fundamental parameter closely related to many physical properties such as elastic constants, specific heat and melting point can be obtained from the average sound velocity (v_m) by the following classical relation [26]:

$$\theta_D = \frac{\hbar}{k_B}\left[\frac{6\pi^2 n}{V_0}\right]^{1/3} v_m$$

where V_0 is atomic volume and v_m the average wave velocity in the polycrystalline material is approximately calculated from the following equation [26]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]^{-1/3}$$

constant. The scatter of all the different points falls within plus or minus 300 K of the following equation for T_m in units of K [28]:

$$T_m = 553\ K + (591/Mbar)\ C_{11} \pm 300\ K$$

The calculated wave velocities (v_t, v_l, v_m), Debye temperature (Θ_D) and melting point (T_m) of studied binary compounds and ternary alloys estimated from elastic constants are listed in Table 2. It is clearly seen from Table 2, the Debye temperature of the considered compounds decrease with increasing atomic number.The high value of the Debye temperature for AlAs implies that its thermal conductivity is to be higher than other studied compounds. The sound velocities are related to the elastic moduli. Therefore, for a material having larger elastic moduli means higher sound velocity. Thermal conductivity, κ, is the property of a material that indicates its ability to conduct heat. So, in order to know if material is a potential candidate for thermal barrier coating application, its thermal conductivity need to be investigated.

Based on the Debye model, Clarke [29] suggested that the theoretical minimum thermal conductivity can be calculated after replacing different atoms by an equivalent atom with a mean atomic mass M/n:

$$\kappa_{min} = 0.87 k_B N_A^{2/3} \frac{n^{2/3}\rho^{1/6}Y^{1/2}}{M^{2/3}}$$

where k_B is the Boltzmann's constant, M is the molecular mass and n is the number of atoms per molecule, N_A the Avogadro's number, ρ the density. The calculated minimum thermal conductivity of studied materials is summarized in Table 2. Table 2 Indicates that the value of minimum thermal conductivity decreases when one moves from Al to In in the compound XAs (Sb) (X=Al, Ga and In). The reduction can be attributed mainly to the difference in Young's modulus, which is a measure of the second derivative of the bonding energy at the

equilibrium interatomic distance x_0, between the studied binary compounds.

Where v_t and v_l are the transverse and longitudinal elastic wave velocities, respectively, obtained using the shear modulus G and the bulk modulus B from Navier's equations [27]:

$$v_t = \sqrt{\frac{G}{\rho}}$$

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}$$

where ρ is the density.

Fine et al. [28] have studied many cubic metals and compounds and have obtained an approximate empirical.

IV. Conclusion

In this study, the structural, mechanical and thermodynamic properties of III-X (X= As, Sb) compounds have been investigated by means of the DFT within Wien2k code. Our results for the optimized lattice parameters (a) and (c) are in good. Agreement with the available experimental data. The elastic constants Cij, and related polycrystalline mechanical parameters such as bulk modulus B, shear modulus G, Young's modulus E and Poisson coefficient σ are calculated using Voigt–Reuss–Hill approximations.

The III-X (X= As, Sb) compound is mechanically stable according to the elastic stability criteria, while no experimental results of elastic moduli for comparison. The calculated Zener factor indicates that III-X (X= As, Sb) compound is elastically anisotropic. The values of the ratio B/G and Cauchy pressure (C12–C44) show a ductile manner for the III-X (X= As, Sb) compound. The polycrystalline III-X (X= As, Sb) turns out to be a low stiff material according to the calculated hardness parameter (H). Finally, from the knowledge of the elastic constants and the average sound velocities, the Debye temperature has been predicted successfully.

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